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(54) Title: **ELECTROCHEMICAL TREATMENT METHOD AND DEVICE FOR SOFTENING WATER**

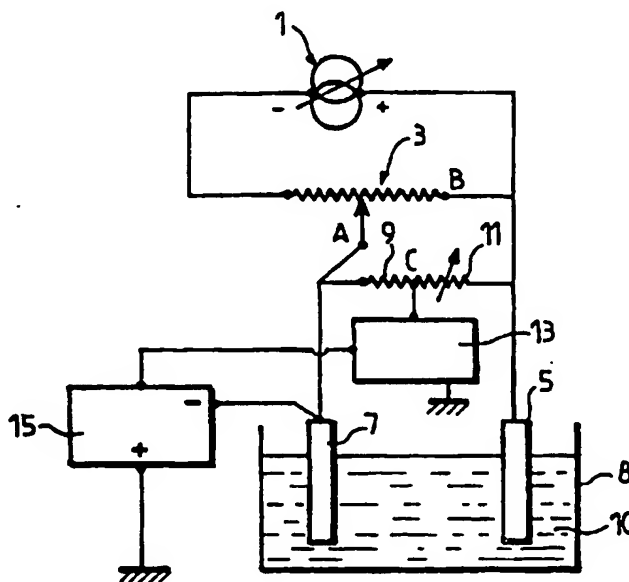
(54) Titre: **PROCEDE ET DISPOSITIF DE TRAITEMENT ELECTROCHIMIQUE DE L'EAU, EN VUE DE SON ADOUCISSEMENT**

(57) Abstract

A method and a device for electrochemically treating water to reduce its degree of hardness, wherein the water to be treated is electrolysed between an anode (5) and a cathode (7, 7') connected to the positive (B) and negative (A) terminals respectively of a current generator (1), each consisting of at least one electrode. A thin porous coating at least partially consisting of calcium carbonate is formed at the cathode (7) and a gas flow is generated through the pores of the cathode (7) as the water is electrolysed so that the crystals at least partially made up of calcium carbonate and formed on said coating during electrolysis are detached therefrom by the gas flow.

(57) Abrégé

La présente invention concerne un procédé et un dispositif de traitement électrochimique de l'eau en vue de la diminution de son titre hydrotimétrique, dans lesquels on effectue une électrolyse de l'eau à traiter entre une anode (5) et une cathode (7, 7'), respectivement reliées aux bornes positive (B) et négative (A) d'un générateur de courant (1), constituées chacune d'au moins une électrode. Suivant l'invention, on constitue à la cathode (7) un revêtement mince et poreux formé au moins en partie de carbonate de calcium et on réalise simultanément une électrolyse de l'eau et la formation d'un flux de gaz, à travers les porosités de la cathode (7), de façon que les cristaux constitués au moins en partie de carbonate de calcium qui se forment sur ledit revêtement au cours de l'électrolyse soient décollés de celui-ci sous l'action dudit flux de gaz.



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ELECTROCHEMICAL TREATMENT METHOD AND DEVICE FOR SOFTENING WATER

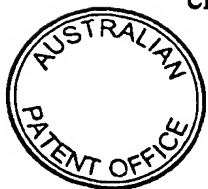
The present invention relates to a method for electrochemically treating
5 water with a view to softening it, as well as to a device for carrying out this method.

Among the various treatments of water with a view to softening it, different methods and apparatus are known, employing a bipermutation of ions on ion exchanger polymers. Treatments are also known, in which there are added to the
10 water to be treated chemical reagents such as lime or soda. In both cases, these techniques employ outside chemical reagents. The use of the latter involves, on the one hand, a substantial modification of the quality of the water and, on the other hand, a regular maintenance and supply of consumable products generating high exploitation costs.

15 Furthermore, different water treatment techniques exist which employ magnetic fields or electric fields. These different known methods have a "delaying" action on the phenomena of scale deposit, provoking the germination of the calcium carbonate within the water and/or intervening on the speed of growth of these germs. The drawback of these water treatment techniques is that
20 they do not provoke crystallization and immediate precipitation of the calcium carbonate contained in the water to be treated.

The present invention aims at overcoming these drawbacks by proposing a method and apparatus making it possible, under particularly economical and reliable conditions, to obtain a total or partial controlled softening of the water.

25 The present invention thus has for its object a method for electrochemically treating water to reduce its degree of hardness, in which the



water to be treated is electrolyzed between an anode and a cathode connected to the positive and negative terminals respectively of a current generator, each consisting of at least one electrode, characterized in that it comprises the steps consisting in constituting at the cathode a thin porous coating at least partially
5 formed by calcium carbonate, simultaneously electrolyzing the water and generating a gas flow through the pores of the cathode, so that the crystals at least partially made up of calcium carbonate and formed on said coating during electrolysis are detached therefrom by the gas flow.

In an embodiment of the invention, the degree of hardness of the treated
10 water may be controlled, particularly in automatized manner, by measuring the value of a given parameter of said water and modifying the value of the intensity of the electric current which traverses the liquid to be treated as a function of the value of said parameter.

The present invention also has for an object a device for electrochemically
15 treating water with a view to reducing its degree of hardness, constituted by an electrolytic cell comprising an anode and a cathode respectively connected to the positive and negative terminals of a current generator, each constituted by at least one electrode, characterized in that the cathode comprises a coating constituted, at least in part, by adhesive and porous calcium carbonate, and means for
20 propelling a gas flow through the pores of this cathode, so as to detach and cause to precipitate the deposits which are formed on said coating, particularly the calcium carbonate deposits.

In an embodiment of the invention, the cathode is constituted by a porous metal, particularly a sintered metal, coated with a thin, porous layer of calcium
25 carbonate.



The jet of gas may be constituted by hydrogen, this latter being obtained in particular by bringing the potential of the cathode to a sufficient given value.

In an embodiment of the device according to the invention, said device comprises means adapted to measure the value of a given parameter of the treated
5 water and means for modifying the value of the intensity of the electric current which traverses the electrolytic cell as a function of the value of said parameter.

Various forms of embodiment of the present invention will be described hereinafter by way of non-limiting example, with reference to the accompanying drawings, in which:

10 Figure 1 is an electric diagram of a water treatment device according to the invention.

Figure 2 is a drawing in perspective of a water treatment device according to the invention.

Figure 3 is a view in longitudinal section of a variant embodiment of a
15 cathode according to the invention.

Figure 4 is a diagram of an embodiment for constituting a cathode covered with a thin, porous coating of calcium carbonate.

Figure 5 is a schematic view of an embodiment of the invention.

Figure 6 is a view in section of a water treatment device according to the
20 invention along line VI-VI of Figure 7.

Figure 7 is a view in section of the device shown in Figure 6 along line VII-VII of the latter.

The device according to the invention shown in Figure 1 is essentially constituted by a current generator 1 which supplies a power potentiometer 3
25 which delivers between its terminals A and B a current of adjustable intensity when they are respectively connected to an anode 5 and a cathode 7 of an



electrolytic tank 8 containing water 10 of which it is desired to reduce the hardness. Terminals A and B of the potentiometer 3 are connected to the two ends of a divider bridge constituted by two resistors, namely a fixed resistor 9 and an adjustable resistor 11 of which a centre point C enables an adjustable
 5 reference voltage to be taken which is supplied to an electronic voltage comparator 13. The latter is connected to an adjustable voltage generator 15 whose positive terminal is connected to earth and negative terminal is connected to the cathode 7, so that it makes it possible to apply thereto an adjustable negative voltage.

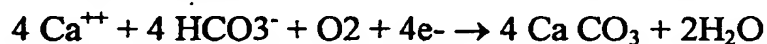
10 As shown in Figure 2, the electrolytic tank 8 is for example constituted by a vat of insulating material of parallelepipedic shape, which comprises at its base a pipe 22 for admission of water to be treated and in its upper part a pipe 24 for evacuation of the treated water. The cathode 7 is constituted by eight plates 7a of stainless steel, preferably of food-compatible type such as the one referenced
 15 316L, which are maintained in spaced apart relationship parallel to one another by nine bars 5a, with the interposition of insulating rings 6, so that these bars constitute the anodes 5. The nine bars 5a are joined together and to an anode terminal 14 by a conductor 12 and the eight plates 7a are joined together and to a cathode terminal 17 by a bar 16. The surface of the plates 7a forming the cathode
 20 7 is polished with care, either mechanically or preferably by an electrolytic polishing. The ratio of the total surface \underline{S} of the plates 7a forming the cathode 7 with respect to the total surface \underline{S}' of the bars 5a forming the anode 5 is of the order of 10 to 20, so that, at the anode, the surface density of the current is from 10 to 20 times greater than what it is at cathode 7. The cathode plates 7a are
 25 spaced apart from one another by about 2 cm. The material constituting the anode 5 is such that the reaction of oxidation of the water is produced without



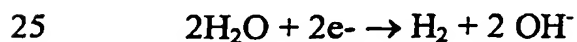
excessive overvoltage. Furthermore, this material must be stable over very long periods. Titanium, and preferably titanium coated with platinum, iridium or ruthenium, will thus preferably be used.

Under these conditions, the present device operates in the manner
5 described hereinafter.

In a first step of the method according to the invention, there is formed on the plates 7a constituting the cathode 7, a fine, porous, so-called primary layer of calcium carbonate. To that end, a first electrolysis of the water is effected, in which the voltage generator 15 is adjusted so that it applies to the cathode 7 a
10 negative voltage, such that the only electrochemical reaction at the cathode is the reduction of the dissolved oxygen, so that a fine, adherent layer of calcium carbonate is then deposited on the cathode in accordance with the reaction:



As the layer of calcium carbonate is formed on the cathode 7, the
15 resistance of the electrolytic cell increases progressively so that the intensity of the electrolysis current decreases, as well as the difference in potential at the terminals A and C of the voltage comparator 13, to attain a predetermined threshold value which was previously fixed by means of the adjustable resistor 11 of the divider bridge. This value is preferably such that it corresponds to a drop in
20 the intensity of the current in the electrolytic cell by 20%. The comparator 13 then controls the voltage generator 15 which applies to the cathode 7 a negative voltage with respect to the earth, which is fixed at a determined value, to provoke at the cathode the reduction of the water, which is translated by a release of hydrogen in accordance with the well-known reaction:



Such release of hydrogen acts on the fine primary layer of calcium carbonate made on the cathode 7 to create pores therein. Consequently, the cathode 7 is ready for the following step during which the degree of hardness of the water contained in the electrolytic cell 8 is reduced.

5 To that end, an electric current is passed in the cell 8 and a higher negative potential is applied, by means of the voltage generator 15, to the cathode 7 in order to provoke a reduction of the water so as to produce a release of hydrogen.

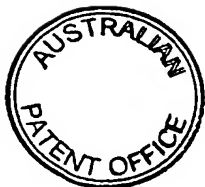
Under these conditions, it is ascertained that the porous layer of calcium carbonate performs the role of centre of nucleation and generates thereon the
10 formation of germs which serve as support for the production of crystals of calcium carbonate during electrolysis, these crystals being torn from the cathode by the stream of hydrogen, so that they then precipitate in the liquid 10 and drop to the bottom of the tank 8, where it suffices to recover them. The calcium carbonate crystals being torn from the cathode 7 as they are formed, the thickness
15 of the primary layer of calcium carbonate remains constant in the course of time and electrolysis may be extended for as long as necessary.

Furthermore, according to the invention, insofar as the density of the anodic current is great, dissolved oxygen is produced in accordance with the reaction:



which drives the carbon dioxide from the treated water and which escapes in the atmosphere.

Moreover, the concentration of dissolved oxygen increases, which promotes the cathodic reaction, since there is addition of the reduction of the
25 dissolved oxygen and of the reduction of the water, which reactions both produce hydroxide ions OH^- .



The method according to the invention may of course be carried out by previously producing cathodes precoated with the primary coating of porous calcium carbonate necessary for carrying out the second step of the method, in the laboratory or in the factory.

- 5 The yield of decarbonation may also be substantially improved in accordance with the invention by forming around the cathode a gel constituted by strongly hydrated calcium carbonate.

To that end, a sufficient negative potential for the surface density of current at the cathode to be greater than $2A/m^2$ is applied to the cathode. In accordance
10 with the present invention, the surface density of the current at the cathode will preferably be included between $2A/m^2$ and $8A/m^2$.

It has been ascertained that, under these conditions, a gel was formed at the cathode which opposed only very weakly the thrust of the hydrogen which originates at this electrode.

- 15 This gel performs two essential functions. Firstly, it behaves substantially like a membrane which exerts a delaying effect with regard to the displacement of the OH^- ions in the solution. The gel also has for an effect to behave like a brake to the migration of the H^+ ions towards the cathode, which reduces the combination of the OH^- ions with the H^+ ions, which combination constitutes a
20 reduction of the yield of decarbonation.

Furthermore, the gel, which is constituted in particular by amorphous monocrystals, attracts the Ca^{++} ions as well as the carbonate and bicarbonate ions. It is ascertained that the OH^- ions do not react directly with the bicarbonate ions but with the H^+ ions released by backscatter, which improves the yield of
25 decarbonation, as, to each neutralization of the H^+ and OH^- in the gel there corresponds the insertion of a Ca^{++} and a CO_3^{--} on a crystal of the gel.



In order to implement the present invention, gases other than hydrogen may be employed. To that end, porous cathodes may be employed, particularly cathodes constituted by a sintered metal. These cathodes are in a first step coated with a porous calcium carbonate layer. As shown in Figure 3, they are constituted
5 by a sintered metal cylinder 7' comprising a central, longitudinal cavity 18 which is in communication, via a conduit 20, with means for supplying pressurized gas. The gas is released through the cathode 7', so that it entrains the calcium carbonate crystals formed thereon in the course of electrolysis.

Of course, in such an embodiment, the voltage generator 15 is no longer
10 used, insofar as it is no longer necessary to provoke at the cathode a reduction of the water with a view to obtaining a release of hydrogen.

The method according to the invention generating carbon dioxide at the anode, the treated water acidifies gradually as treatment continues. The reduction of the pH thus makes it possible to control, as set forth hereinafter, the process of
15 decarbonation of the water.

The decarbonated water thus produced, insofar as it is not desired to use its aggressive character (as set forth hereinafter) with respect to the CaCO_3 , must therefore undergo a treatment intended to eliminate the carbon dioxide. To that end, known methods of mixing, eddy, trickling, etc... may be used.

20 In order to constitute the primary calcium carbonate coating on the cathode 7, a device as shown in Figure 4 may be employed.

In this Figure, the device is constituted by a support of sintered metal, intended to constitute the cathode, having the shape of a bell 21. This bell 21 is immersed in a tank 23 supplied with carbonated water via a lower pipe 25. The
25 tank 23 comprises an upper pipe 26 which acts as overflow. An electric resistor 28 is disposed inside the bell 21, and a pipe 30 communicates the interior thereof



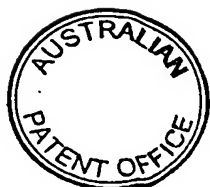
with the interior of the tank 23. To obtain on the surface of the porous bell 21 a porous deposit of calcium carbonate, operation is as follows:

The electric resistor 28 is supplied with electric current so as to take the water contained in the tank 23 to boiling point. In the course of this operation, a
5 calcium carbonate deposit is formed on the walls of the bell 21, and in particular on the outer walls thereof. The bubbles of steam formed in the bell 21 traverse its sintered metal walls to be released to the outside, traversing the fine coating of calcium carbonate formed, which creates pores therein. When the thickness of the porous coating of calcium carbonate is sufficient, the process is interrupted and a
10 cathode coated with a thin, porous layer of calcium carbonate is thus available. The pipe 30 makes it possible to remove water already treated, therefore partly deprived of its calcium carbonate, to produce the bubbles of steam, this minimizing the quantity of calcium carbonate formed inside the bell 21.

Of course, each anode and each cathode may be constituted by any number
15 of elements.

When the layer of porous calcium carbonate is formed on a sintered metal, and more generally on a porous metal, this layer of calcium carbonate may be used as filtration membrane, whether it be in the case of it being produced by thermic effect or by electrolysis. The release of gas through the layer of calcium
20 carbonate may easily be interrupted regularly in order to use the pores of this layer as passage for the water to be filtered. A simple system for avoiding blocking of the pores consists in alternating the operations of filtration and of release of gas.

The present invention makes it possible to control, particularly
25 automatically, the level of decarbonation of the water. To that end, a physico-chemical parameter of the water is permanently measured during electrolysis and,



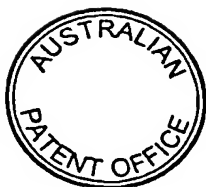
as soon as this parameter attains a predetermined value representative of the state of decarbonation of the water, one intervenes on the process. In this way, the pH of the water may be measured and the electrolysis stopped as soon as it attains a given value. Intervention on the process of electrolysis may also be progressive, .
5 and, as the pH of the treated water decreases, the electrolysis current may be progressively reduced, cutting it totally when a given platform value is attained.

Figure 5 thus shows a device according to the invention comprising a sensor 36 which is disposed on a pipe 38 downstream of an electrolytic cell 40 and which is connected to an analysis unit 42. This latter compares the parameter
10 measured by the sensor 36, particularly the pH, the conductivity, etc... with a reference value recorded in the analysis unit 42. The latter is in relation with an interface 44 adapted to intervene on the intensity of the current which traverses the electrolytic cell 40 in order to correct it as a function of the measure made by the sensor 36.

15 One of the parameters particularly appropriate for the control of the degree of hardness of the water is the pH, by reason, on the one hand, of its close correlation therewith and, on the other hand, of the easy measurement thereof.

Of course, the method and the device according to the invention make it possible, jointly with the crystallization of the calcium carbonate, to ensure
20 precipitation of other salts, particularly salts of iron sodium, manganese, etc..., all these reactions being able to lead to a partial purification of the water or more exactly to a more complete demineralization thereof. The present invention is thus advantageous for treating brackish or ferriferous water.

In a variant embodiment, the present invention may also be carried out in a
25 lamellar decanter device.



For example, a device of this type has been shown in Figures 6 and 7, constituted by a closed tank 50 comprising in its upper part a pipe 52 for admission of the water to be treated. The interior of the tank 50 is divided into two chambers, namely an inlet chamber 54 of small volume and a treatment
 5 chamber 58, by a transverse partition 56 which extends from the upper part of the tank 50 to such a distance from the bottom thereof as to allow a communication of the inlet chamber 54 with the treatment chamber 58. The interior of the treatment chamber 58 comprises a series of twelve transverse plates 59 inclined with respect to the vertical and which are maintained in their lower part by
 10 longitudinal elements 60 and in their upper part by longitudinal elements 62. The upper part of the inclined plates is in communication with an overflow device 64 connected to a pipe 66 for evacuating the treated water.

The plates 59 are constituted by a metal, and particularly stainless steel, and are joined together by a longitudinal rod 68 so that they constitute as many
 15 electrodes forming the cathode 7 of the device according to the invention. Metal wires 70 are stretched between each of the lower (60) and upper (62) elements, between the plates 59. All the wires 70 of the same longitudinal element are joined together by a longitudinal wire 72, the different longitudinal wires 72 being connected together by a transverse wire 74, so that the different wires 70
 20 constitute as many electrodes forming the anode 5 of the device. The different wires 70 forming the anode 5 will preferably be constituted by titanium containing iridium.

Such a device is particularly advantageous in that it combines the normal effect of a decanter with that of the water treatment according to the invention.
 25 This device is also particularly efficient in that it combines a large electrode surface and a considerable volume of degassing.



In a particularly advantageous embodiment of the invention, the yield of decarbonation is increased by removing part of the hardness of the water to be treated by passing the latter through a fluidized bed constituted by crystals formed essentially by the calcium carbonate extracted from the water in the course of treatment. Such a passage may also be effected from the water already treated.

All the parts of the cathode may advantageously be produced with the aid of vitreous carbon or silver, which makes it possible to reduce the dissolved oxygen possibly in excess in the water during its passage in the treatment cell.

According to the invention, the demineralized water thus obtained may be used with a view to punctually or periodically removing scale from installations, particularly installations employing boilers. Timing systems may thus be used which allow the boiler to function normally during the day and which, at night, control bypass means for circulating the water previously treated in the pipes of the boiler and its accessories. In this way, scaling of the circuits of this boiler is considerably reduced by periodic dilution of the scale formed.



The claims defining the invention are as follows:

1. Method for electrochemically treating water to reduce its degree of hardness, in which the water to be treated is electrolysed between an anode and a cathode connected to the positive and negative terminals respectively of a current generator, each having at least one electrode, the method including the steps of:
 - constituting at the cathode a thin porous coating at least partially formed by calcium carbonate,
 - simultaneously electrolysing the water and generating a gas flow through the pores of the cathode, so that the crystals at least partially made up of calcium carbonate and formed on said coating during electrolysis are detached therefrom by the gas flow.
2. Method according to claim 1, wherein the gas flow is a flow of hydrogen.
3. Method according to claim 1 or 2, characterised in that, in the course of implementing said method, the potential of the cathode is taken to a sufficient given value to provoke, at this electrode, a release of hydrogen.
4. Method according to claim 1, 2 or 3 wherein the potential of the cathode is such that the surface current density at the cathode is included between 2A/m^2 and 8A/m^2 .
5. Method according to any one of the preceding claims, wherein the value of a given parameter of the treated water is measured and the value of the intensity of the electric current which traverses it is modified as a function of the value of said parameter.
6. Method according to claim 5 wherein said parameter is the pH.
7. Method according to any one of the preceding claims, characterised in that the crystals constituted at least in part by calcium carbonate are collected so as to form a bed and the water to be treated and/or the treated water is made to pass through this bed.



8. Device for electrochemically treating water with a view to reducing its degree of hardness, constituted by an electrolytic cell including an anode and a cathode respectively connected to the positive and negative terminals of a current generator, each having at least one electrode, wherein the cathode includes a coating constituted, at least in part, by adhesive and porous calcium carbonate, and means for propelling a gas flow through the pores of this cathode, so as to detach and cause to precipitate the deposits which are formed on said coating, including the calcium carbonate deposits.
9. Device according to claim 8, wherein the ratio of the surface of the cathode with respect to the surface of the anode is included between 10 and 50.
10. Device according to one of claims 8 or 9, characterised in that the cathode is constituted by a porous metal coated with a thin, porous layer of calcium carbonate.
11. Device according to claims 8 to 10, wherein the metal of the cathode is a sintered metal.
12. Device according to any one of claims 8 to 10, wherein the cathode is constituted by a metal whose outer surface is polished.
13. Device according to any one of claims 8 to 12, characterised in that the cathode is constituted, wholly or partly, by vitreous carbon or silver.
14. Device according to any one of claims 8 to 14, including means for propelling a gaseous flow of hydrogen through the cathode.
15. Device according to claims 8 to 14, including electrical supply means adapted to take the potential of the cathode to a sufficient given value to provoke, at this electrode, a release of hydrogen.



16. Device according to claim 15, wherein said electrical supply means are such that the surface current density at the cathode is included between 2A/m^2 and 8A/m^2 .
17. Device according any one of claims 8 to 15, including means adapted to measure the value of a given parameter of the treated water and means adapted to modify the value of the intensity of the electric current which traverses the electrolytic cell as a function of the value of said parameter.
18. Device according to any one of claims 8 to 17, characterised in that the anode is constituted by titanium coated with a material such as platinum, iridium or ruthenium.
19. Method for electrochemically treating water substantially as hereinbefore described with reference to the drawings.
20. Device for electrochemically treating water substantially as hereinbefore described with reference to the drawings.

Dated this 28th day of April 1999

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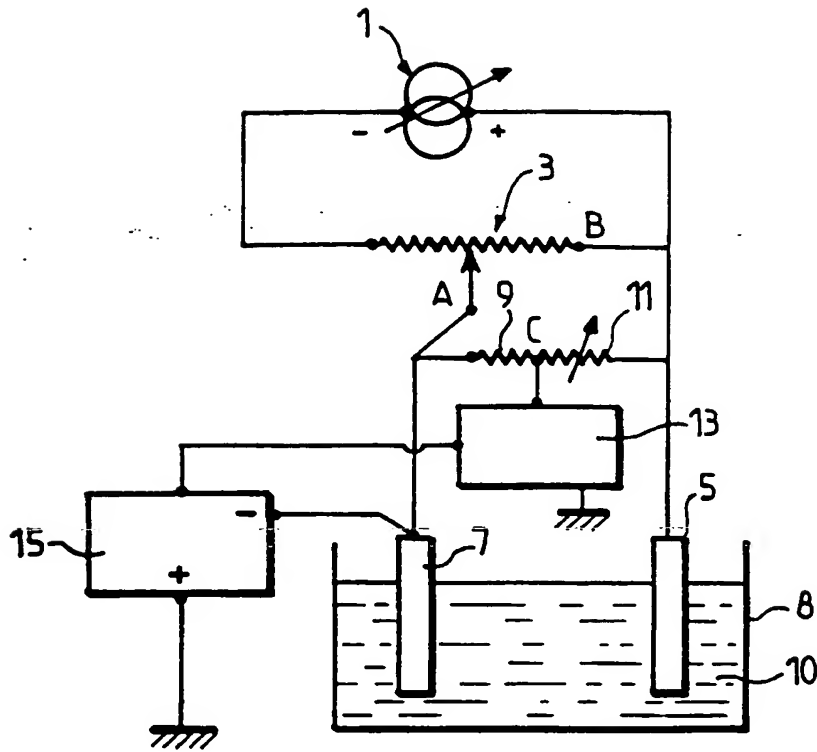


FIG. 1

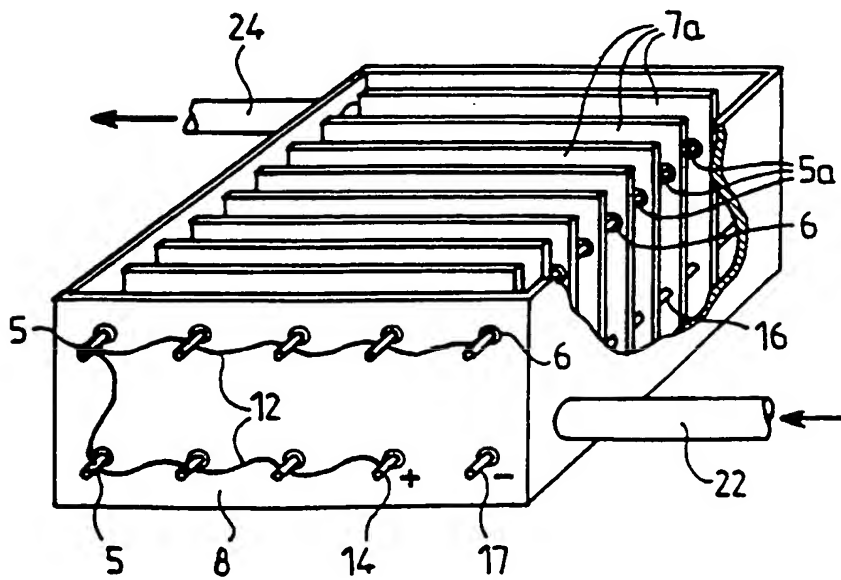


FIG. 2

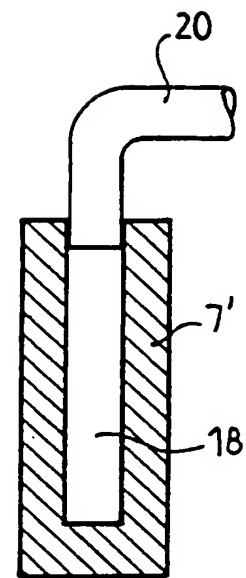


FIG. 3

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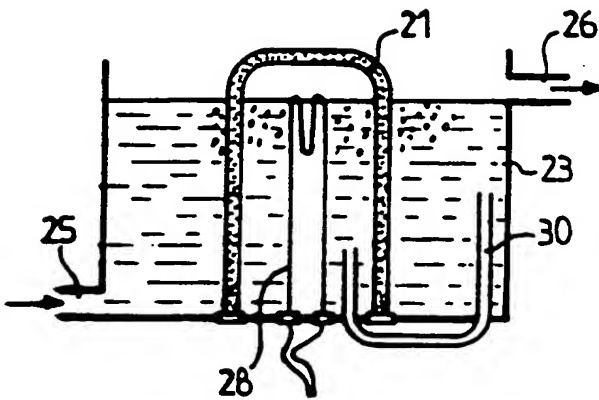


FIG. 4

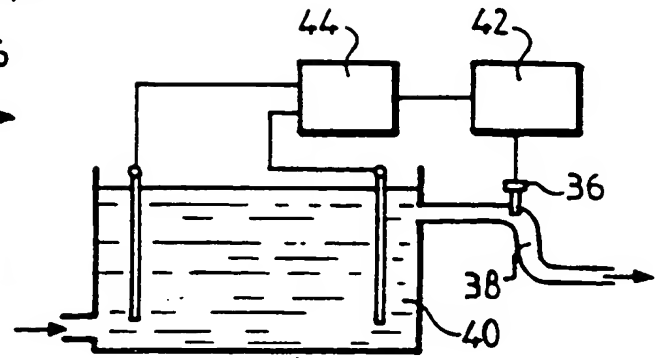


FIG. 5

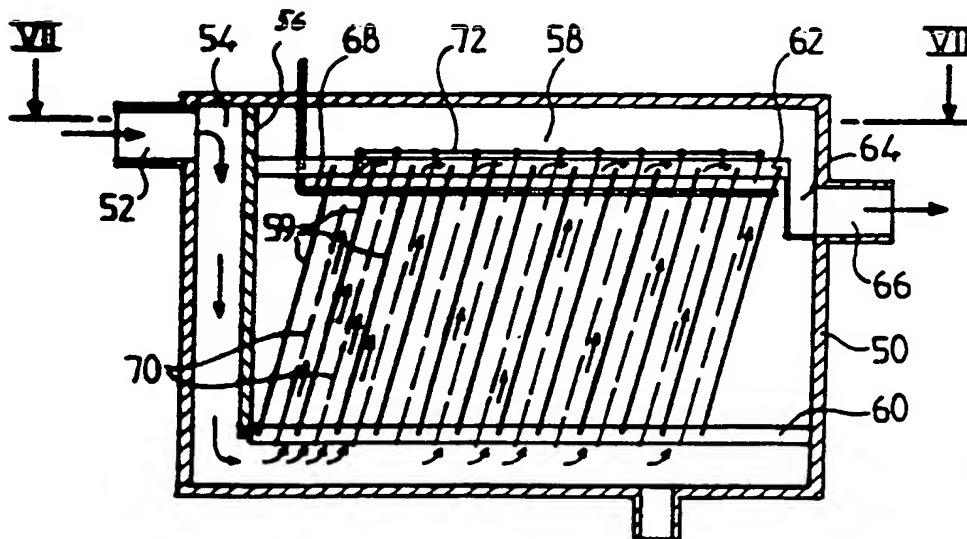


FIG. 6

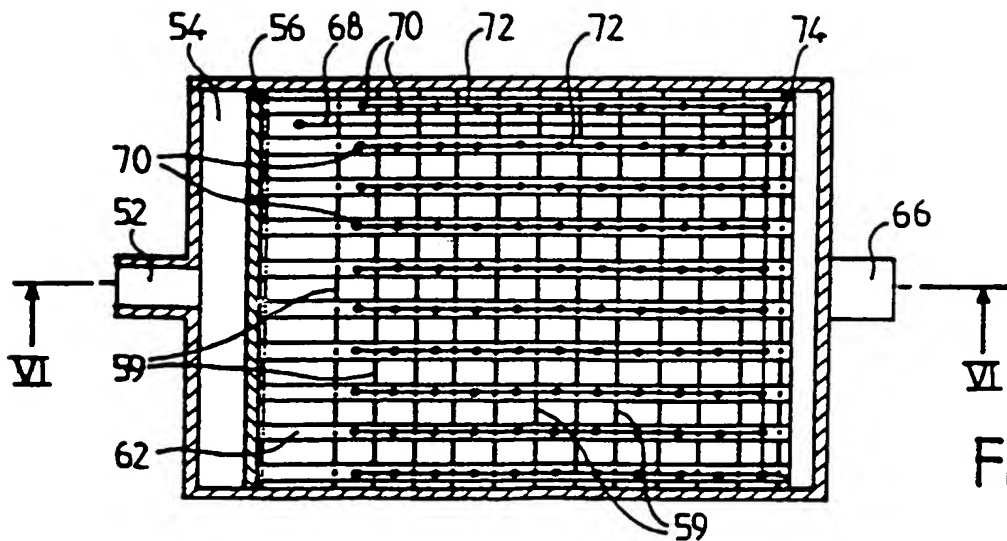


FIG. 7